

Research Article

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Synthesis and characterization of nano-amendment for effective remediation of soil acidity

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Summary

Industrialization and climate change had increased soil acidity which deteriorated the soil health and reduced crop productivity through release of toxic concentration hydrogen and aluminium, manganese and iron. Acid soils ($\text{pH} < 5.5$) are extensively found in region of high rainfall, temperature and hilly region. Liming of acid soils the changes ($\text{pH} 5.5$ to 6.5), rectifies adverse effects and also improves the soil fertility. But large quantity of lime used (7.2 tons per acre). In order to optimize the rate of lime nano technological approach was used. Naturally available micro-size conventional calcium carbonate particles were used for synthesis of nano crystals through physical method of top down approach, using high energy ball milling (HEBM) with different hours and encapsulated with non-ionic surfactant (1% chitosan). It produced uniform nano sized particles (nano-lime), which were characterised using particle size analyser (approximately $115 - 120$ nm), zeta potential (-50 mV), powder X-ray diffraction (d spacing 3.13). It confirmed that presence of Ca and Mg with Raman Shifts ($713, 1086$ cm^{-1}) and Fourier transform infrared spectroscopy (844.7 cm^{-1}). Shape and structure was observed through scanning electron microscopy (SEM) and transmission electron microscopy (TEM). Synthesized of calcium carbonate nano crystalline particles were environment friendly. Reduced particle size and increased surface area where offered an opportunity for reclamation of soil acidity as an amendment and can be scaled up for agricultural production.

Key words : Acid soils, Lime, Nanotechnology, High energy ball milling

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Introduction

Occurrence of acid soils in Indian subcontinent is highly varied in nature and it is due to wide variation of climatic conditions. Soil acidity is caused by free release of hydrogen, aluminium, manganese and iron toxic concentration (Das, 1996). It is estimated that of approximately 49 Mha are acid soils ($\text{pH} 4 - 5.5$) (Biswas and Mukherjee, 2002). In acid soils, free release H^+ and Al^{3+} concentrations become toxic to plant root growth

and root exudates. Historically limestone (pure calcium carbonate) application is the most common management practice, which is used to neutralize the toxic concentrations of H^+ , Al^{3+} , Mn, Fe and increase the exchangeable Ca and Mg (Adams, 1984). Pure crystalline CaCO_3 is called calcite or calcitic limestone and has a neutralising value of 100 per cent. Limestone is only slightly soluble in pure water, but if the water is saturated with carbon dioxide at ordinary temperatures, it is soluble

to the extent of about one part by weight in 1000 parts of water, forming bicarbonates. The carbonate forms in finely divided form may also react directly with soil colloids. The colloids are thus charged with bases, where reaction is accompanied by the liberation of carbon dioxide. It also modifies the soil property and improves nutrient availability for root growth. Usually, plants grow well at a pH range of 6.5-7.5 due to the optimum availability of essential nutrients and liming is an important to maintain the pH at this range. Liming enhances the physical (structure), chemical (essential nutrients) and biological (microbial population) properties of soil through its direct effect on the amelioration of soil acidity and indirectly promotes root distribution.

The effectiveness of agricultural limestone also depends on the neutralizing value, physical properties and particle size (Brady and Weil, 2008). The rate of reaction of liming materials with acid soils depends upon its fineness because finer materials increase the surface contact with the soil. If the liming materials are coarse, the rate of reaction will be slight (Alley *et al.*, 1980). The amount of finer fraction of liming materials will be required much less as compared to coarser fractions of the material to achieve a certain pH. In this example, a 100-mesh lime material (100% efficient). Particle size or fineness, determines the reaction rate which depends on the surface area in contact with the soil (Meyer and Volk, 1952).

Nano-technology deals with small particles with the dimension of 1-100 nm. Nano particles with extremely high reactivity and deliverability can be applied as amendments to improve soil quality, mitigate soil contaminations. These particles have high surface mass ratio and are capable of improving the agricultural inputs. Such as nano-gypsum reclaimed alkaline soil (Santhosh Kumar, 2012). Nano-technology applications in agriculture are gradually transforming the theoretical possibilities into the practical applications (Subramanian and Tarafdar, 2011). The role of nanotechnology in soil reclamation is yet to be attempted.

With the above background, present study was carried out to synthesis the nano lime and its structural characterization by using various spectroscopic as well as microscopic studies. Also present study was aimed to determine the effects of synthesized nano-lime on soil acidity reclamation under laboratory conditions.

Resource and Research Methods

Agricultural lime used in this study was calcite (CaCO_3), purchased from GM chemicals, India. Other reagents and chemical were purchased from Merck, Mumbai, India.

Physical and chemical analysis of acid soil :

Physical and chemical properties of the acid soil were assessed through the standard protocols of soil analysis. The results of the soil analysis are shown in Table A.

Table A : Physico - chemical properties of acid soil

Sr. No.	Particulars	Contents of various parameters evaluated
I	Physical properties	
1.	Mechanical analysis	
	Clay (%)	33.4
	Silt (%)	20.2
	Fine sand (%)	28.6
	Coarse sand (%)	17.0
2.	Textural class	Sandy loam
3.	Soil series	
4.	Physical constants	
	Bulk density (Mg m^{-3})	1.42
	Particle density (Mg m^{-3})	2.65
	Pore space (%)	35.71
	Hydraulic conductivity (cm hr^{-1})	0.44
II	Physico-chemical properties	
1.	pH (1:2.5 soil: water)	5.2
2.	EC (dSm^{-1})	0.32
III	Chemical properties	
1.	Organic carbon (g kg^{-1})	0.318
2.	CEC ($\text{C mol (p+) kg}^{-1}$)	11.5
3.	Available nitrogen (kg ha^{-1})	256
4.	Available phosphorus (kg ha^{-1})	9.52
5.	Available potassium (kg ha^{-1})	352
6.	Exchangeable calcium ($\text{C mol (p+) kg}^{-1}$)	2.4
	Exchangeable magnesium ($\text{C mol (p+) kg}^{-1}$)	2.51
7.	Total calcium (%)	0.280
8.	Total magnesium (%)	0.202
9.	pH of soil buffer suspension	5.2
10.	Lime requirement (tonnes /acre)	8.6-10

Synthesis of nano-lime :

Nano-crystalline lime particles were synthesized

using a high energy ball milling (Fritsch-pulverisette 7, Germany) at dry condition with milling speed (600 rpm), duration (6 hours) and balls to powder ratio was set as (1:10), respectively (Manikandan *et al.*, 2013 and Thirunavukkarasu, 2014). Surface modification of ball milled sample was done using a biodegradable polymer (Chitosan 1% in acetic acid) as 2:1 W/V (nano-lime : Chitosan) basis with continuous stir for 30 minutes (Li, 2003; Subramanian and Sharmila Rahale, 2012 and Santhosh Kumar, 2012). After surface modification nano-lime was dried and powdered for further characterisation.

Characterization of surface modified nano-lime :

Characterization of nano-lime was undertaken using particle size analyser (PSA) (Horiba Scientific Nano partica SZ-100), X-ray diffraction (XRD) patterns by Powder XRD (Bruker D8 Advance Powder X-ray Diffractometer, Germany), Fourier-transform infrared spectroscopy (FT-IR) by Shimadzu Model-FTIR, Raman Spectroscopy by (R-3000 QE TM), scanning electron microscopy (SEM) and Energy dispersive X-ray spectroscopy (EDS) by SEM (FEI Quanta 250) estimated as per standard procedure (Das and Ansari, 2009; Manikandan and Subramanian, 2014). All graphs are prepared using Microcal origin 6.0 software.

Percolation study to assess the efficiency of nano-lime :

The percolation reactor was designed in order to assess the efficacy of nano-lime in a column of soil with a constant flow of solution as fabricated by (Hernandez

et al., 1994). The percolation reactor consists of a cylinder (internal diameter of 2.5 cm and height of 15 cm) through the top of which de-ionized water is continuously pumped at a flow rate of 50 ml per day. In this technique, a column of test soil was loaded in a sample chamber. About 1 g of nano-lime homogenised with varying levels of soil column. The leachate was collected from the 5th day for a period of 60 days at an interval of 5 days. The Ca^{2+} content was measured in the leachate regularly (Jackson, 1973) to assess the efficiency of nano-lime.

Research Findings and Discussion

Nano sized (approximately 115-120 nm) particles of lime were obtained after 6 h of ball milling (Fig. 1). It got reduced from 1000 to 115 nm and encapsulation of chitosan increased the particle size. The reduction size is due to grinding action of balls on lime under dry condition. Similar results were observed in biochar and zeolite by Manikandan *et al.* (2013) and Thirunavukkarsu (2014). This top down approach has facilitated extensive surface area for adsorption of cationic nutrients and anionic nutrients on surface modification of the lime with cationic surfactant. Surface modification helps in stability of synthesized nano particles of lime. Our study had clearly shown the zeta potentials (-50.9 mV) (Fig. 2). The particles range of +30 to +60 and -30 to -60 indicating the highly stable minimal aggregation. The above obtained results are in confirmation with that of Santhosh Kumar (2012).

Raman spectroscopy is a form of vibrational spectroscopy, much like infrared spectroscopy. A raman

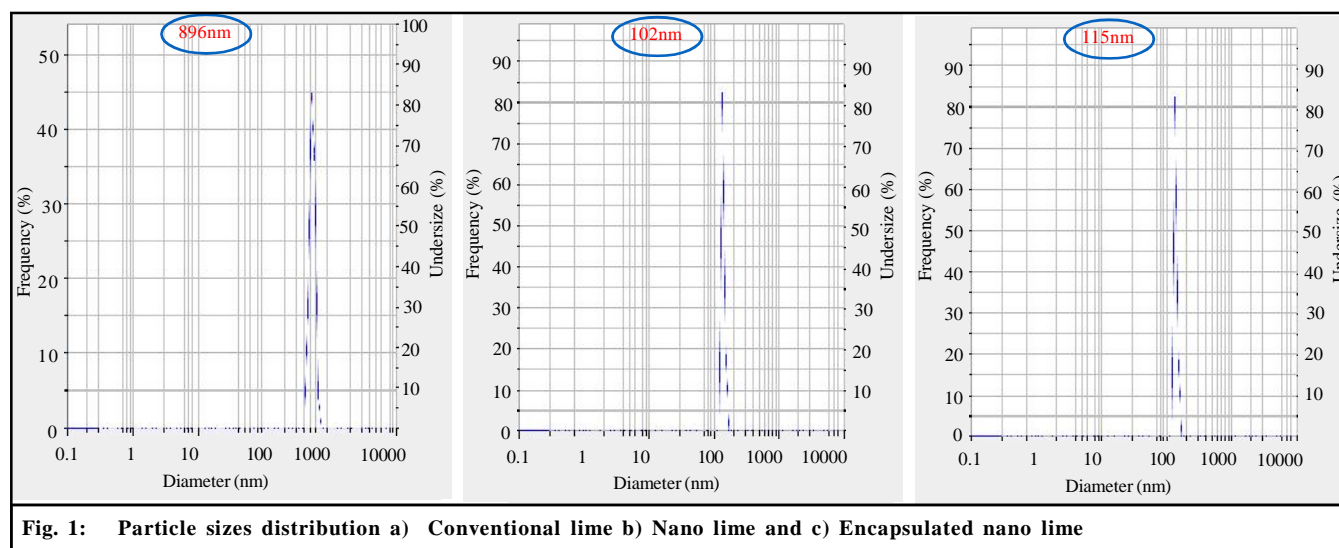


Fig. 1: Particle sizes distribution a) Conventional lime b) Nano lime and c) Encapsulated nano lime

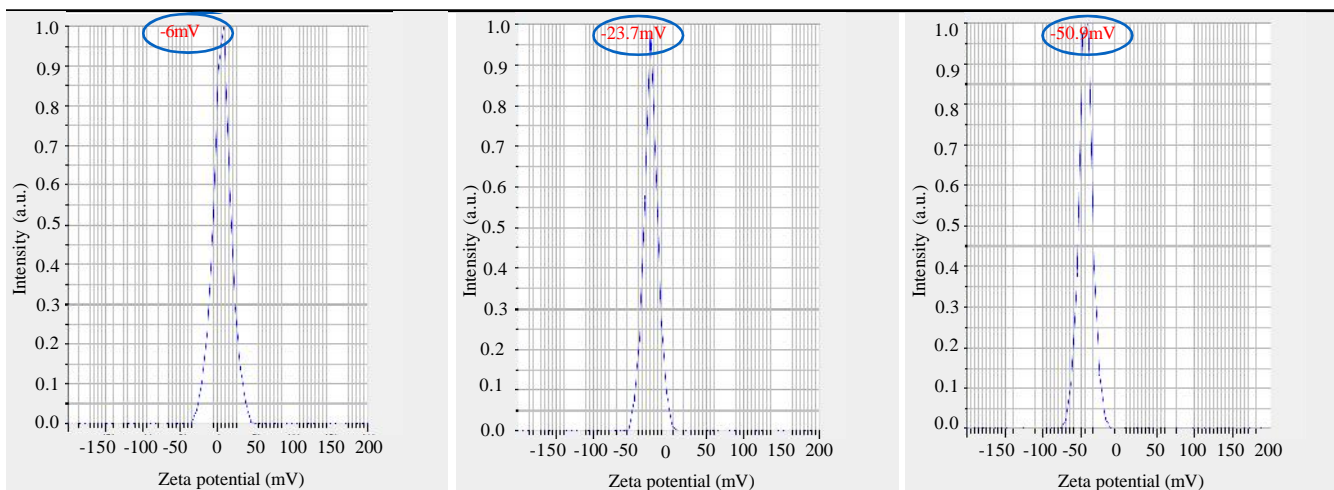


Fig. 2: Zetapotential of a) Conventional lime, b) Nano lime and c) Encapsulated nano lime

spectrum is a plot of the intensity of raman scattered radiation as a function of its frequency difference from the incident radiation (Schrader, 1995). The data on Raman shift peak values confirmed for nano-lime is given Fig. 3. The broad signal collected at 282, 713, 1086 and 1325 cm^{-1} for nano lime, respectively. The data is useful for chemical analysis for several reasons.

X-ray powder diffraction is a non-destructive technique widely applied for the characterization of crystalline materials. Results are commonly presented as peak positions at 2θ and X-ray counts (intensity) in the form of x-y plot (Bish and Post, 1989). The data

confirmed with XRD peak values which are given Fig. 4. The 2θ values shows 26.2, 21.64, 30.58, and 23.84 for nano lime, that corresponded to d spacing = 2.89, 3.97, 3.33, and 3.96 \AA , respectively.

The average modern infrared instrument records spectra from 400-4000 cm^{-1} . The data confirmed with FT-IR spectra which are given in the Fig. 5 which has characteristic peaks of nano lime shows 844.77, 1172.65, 1838.06, 2245.03, 2313.52. This group frequencies help to characterize a compound, and the combination of the bands associated with these group frequencies and the skeletal frequencies are used to identify a specific

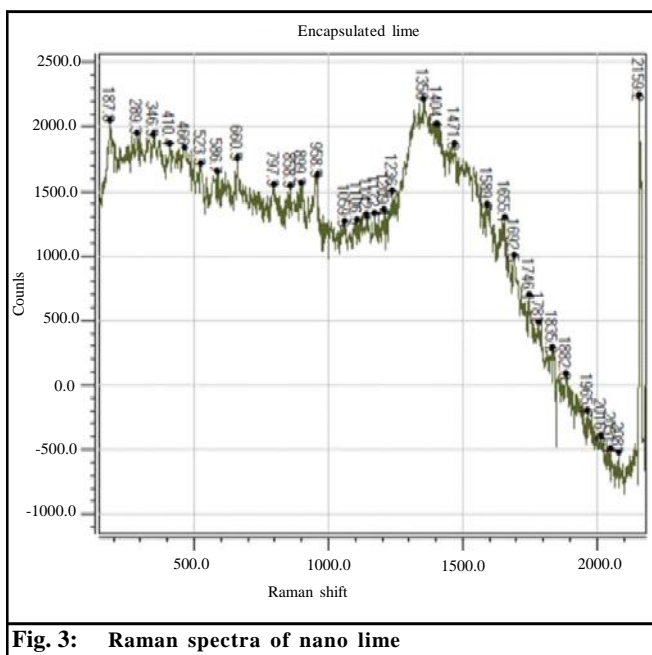


Fig. 3: Raman spectra of nano lime

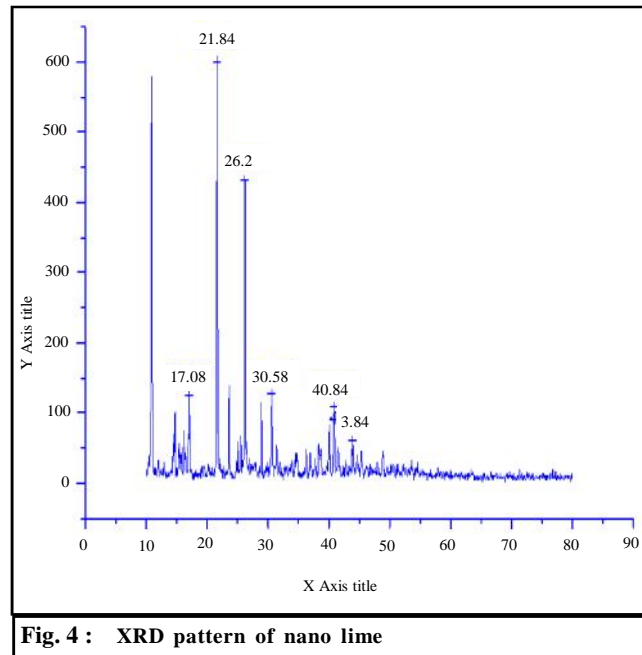
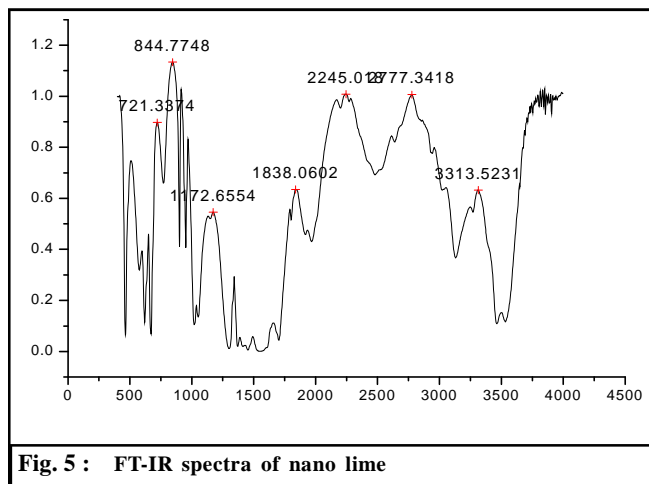


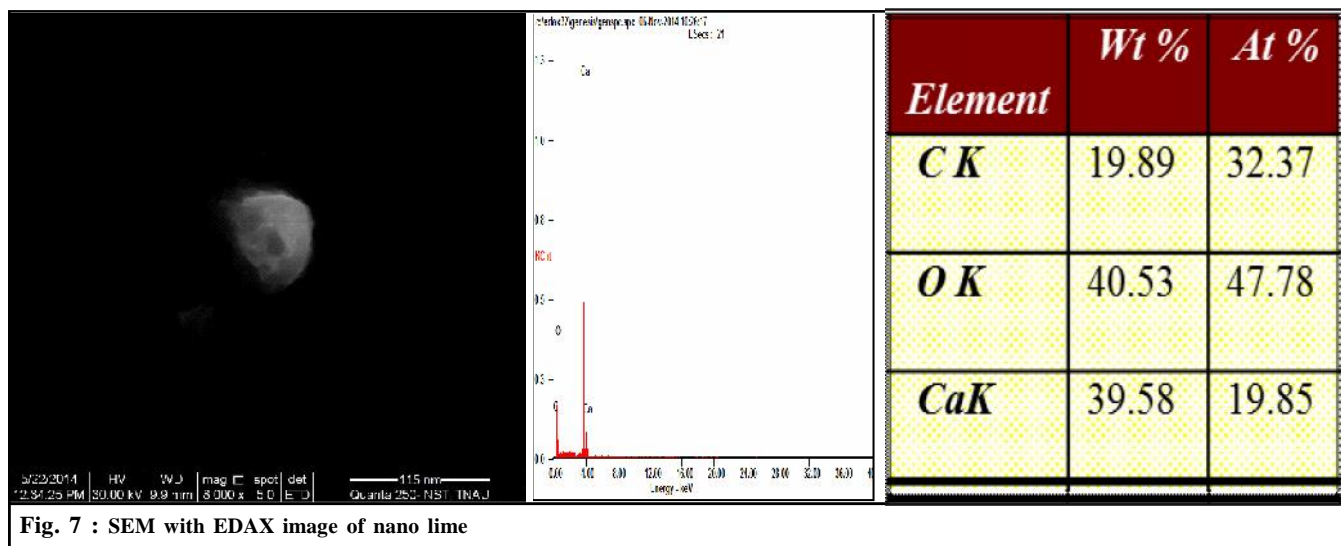
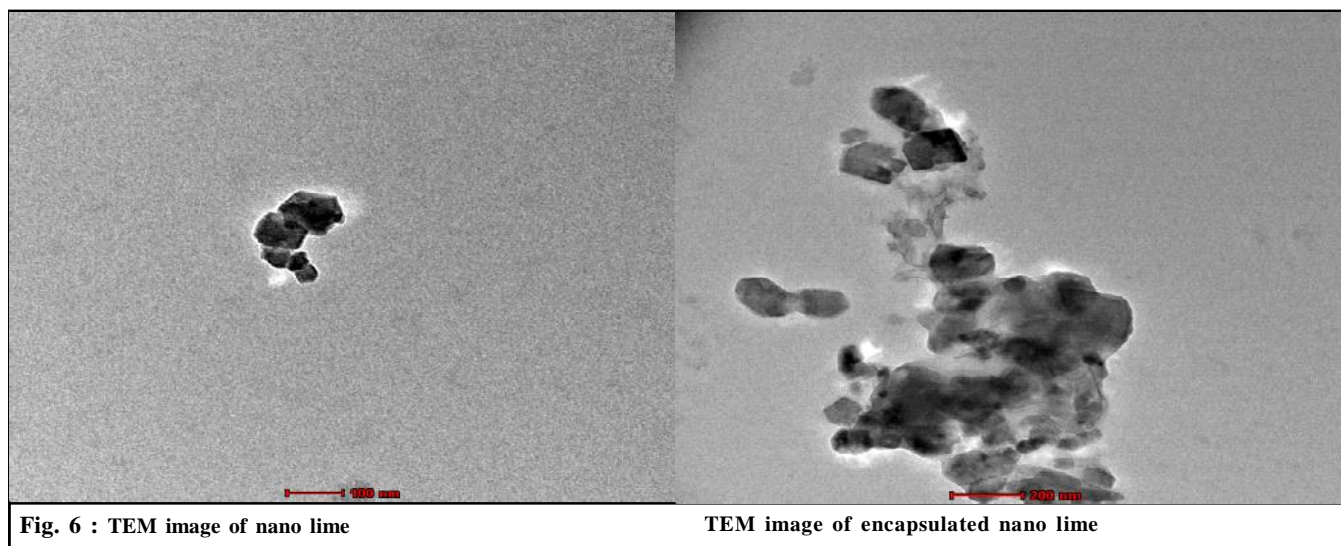
Fig. 4: XRD pattern of nano lime



compound (Smith, 1999).

The characteristics of nano-lime performed using high resolution microscope *viz.*, SEM and spectroscopy clearly indicated the successful synthesis of nano-lime. The SEM image of nano-lime was clustered and consolidated while its carrier, chitosan is scattered and sparse. The Raman spectra and FTIR which measures the functional groups of nano materials have confirmed the presence of lime loaded into the chitosan as depicted by the presence of functional groups. Further, the XRD picture showed the reduction in d-spacing that coincide with ion attachment between the lattices.

The efficiency of nano-lime was examined using the percolation reactor. The data on Ca^{2+} of the leachate



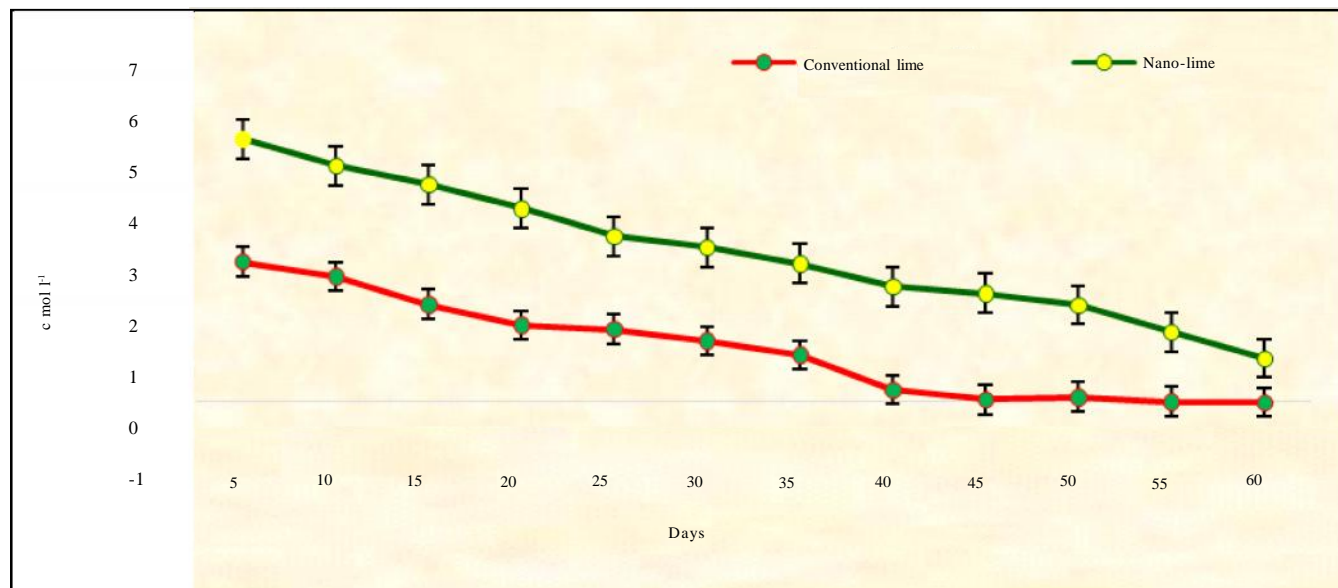


Fig. 8 : Amount of exchangeable calcium from nano-lime (Percolation study)

clearly showed that, the Ca^{2+} content declined proportionately with the progress of the experiment. Initially, the Ca^{2+} content measured was in the range of 5.18 me l^{-1} , while in the last stage of the experiment (55-60 days), the Ca^{2+} content was reduced to a minimum of 0.2 to 0.4 me l^{-1} (Fig. 7). The Ca^{2+} concentration almost ceased to exist in the leachate at the end of the experimental period. Nano-lime possesses extensive surface area and adsorptive sites to exchange Ca^{2+} with Al^{3+} and H^+ in the soil exchangeable complex. Since nano-lime efficiently retained Ca^{2+} Wednesday, 06 January 2016 and displaced, Al^{3+} and H^+ , the Ca^{2+} content of the leachate linearly declined with the progress of the experiment. The study further indicates a long lasting effect of nano-lime to regulate the retention of Ca^{2+} in the chitosan, while having considerable low amounts of Ca^{2+} in the solution. The data corroborate with the observations of our pot culture experiment, where the leachate of surface drainage were determined for the concentration Ca^{2+} and Al^{3+} and H^+ ions (Fig. 8).

Conclusion :

It is concluded that the after encapsulation of nano lime with chitosan the particle size slightly increased and zeta potential of encapsulated nano lime particles getting stability. Raman spectroscopy, FTIR and XRD study confirmed the calcium attachment in the surface modified nano-lime. SEM and TEM images showed trigonal shape of calcium particles. Finally, the percolation reactor study

showed that amount of exchange Ca^{2+} released from encapsulated nano lime was extensive surface area and adsorptive sites to exchange Ca^{2+} with Al^{3+} and H^+ in the soil exchangeable complex. Since nano-lime efficiently retained Ca^{2+} and displaced Al^{3+} and H^+ the Ca^{2+} content of the leachate linearly declined with the progress of the experiment. The study further indicates a long lasting effect of nano-lime to regulate the retention of Ca^{2+} in the chitosan complex, while having considerable low amounts of Ca^{2+} in the solution.

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